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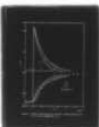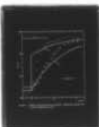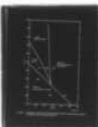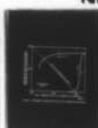   SEP 78   C M ABLOW, B J WOOD, H WISE   F49620-77-C-0123
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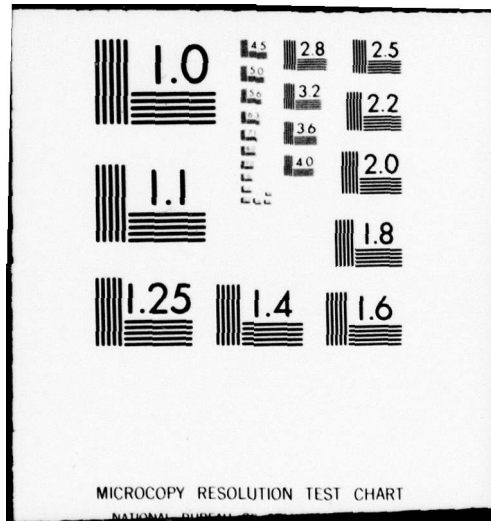
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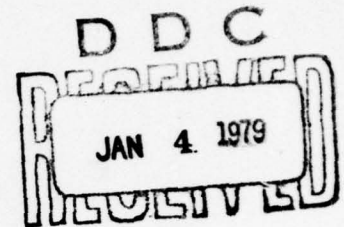
CONTRIBUTION OF SURFACE CATALYSIS AND
GAS PHASE REACTION TO CATALYTIC COMBUSTOR PERFORMANCE

By: C. M. Ablow, B. J. Wood, and H. Wise

Approved:

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I INTRODUCTION

Catalytic monolith combustor are under development for efficient combustion of fuel-air mixtures in air-breathing thrustors. However current engineering design has encountered unstable operating ranges leading to blow off at high power and extinction at idle. To overcome these difficulties a better understanding is required of reactive flow with exothermic reaction on catalytic reactor walls and in the gas phase. The objective of our research effort is a detailed theoretical analysis and experimental study of the various parameter affecting the catalytic combustion process. Of special concern is a quantitative assessment of the contributions of homogeneous (gas-phase) reaction and heterogeneous (wall) reaction to monolith combustor performance.

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II THEORETICAL ANALYSIS

We have developed a theoretical model on the basis of which
temperature and reactant/product distribution can be calculated in a
tubular duct with catalytic walls. Under conditions prevailing in the
central ducts of a monolith combustor, the model provides an analytic
solution which proves useful in examining the role of various operating
parameters on combustor performance. The theoretical work and its
application to experimental data is described in detail in the attached
report (Appendix) entitled: "Theoretical Analysis of Temperature
and Composition in a Catalytic Monolith Reactor."

In this model we assume plug flow at constant pressure and take
average constant values for the transport parameters. Axial conduction
of heat in the gas and in the duct wall is neglected in comparison with
convection in the gas and radial conduction through the wall to the
surroundings. The model uses global reaction kinetics with first-order
dependence of the reaction rate on the fuel concentration in the presence
of excess air. These kinetic parameters are obtained from separate
studies of the platinum-catalyzed oxidation of various hydrocarbon fuels
at concentrations and catalyst temperatures in the same range as employed
in catalytic monolith combustion. The theoretical model is developed
in nondimensional form so that governing parameters can be identified.
These include the reduced activation energies and Damkohler numbers for
the gas phase and catalyst wall reactions, the Stanton number for heat
transfer between the gas and duct wall, the Lewis number ratio of gas
transport coefficients, and the ratio of the inlet gas temperature to
the theoretical temperature rise under adiabatic conditions.

An analytic solution has been obtained for the adiabatic case where no heat is exchanged through the duct walls, a condition closely approximated in the central section of a catalytic monolith reactor. The solution relates temperatures and concentrations at the wall and in the stream that can exist at any cross section of the duct. From this phase-space solution one can readily obtain parameter ranges where the wall reaction is controlled by surface kinetics or by diffusion, where the gas phase reaction makes a contribution, or where multiple responses can occur.

Ducts on the periphery of the monolith exchange heat with their surroundings. In this nonadiabatic case the temperatures and concentrations are so coupled to distance down the duct that the differential equations of the model generally require numerical solution. We have obtained analytic solutions in the limiting case of wall reaction controlled by diffusion and negligible gas phase reaction.

The model is applied to experimental data for the platinum catalyzed combustion of propylene-air and hydrogen-air mixture. The agreement observed between theory and experiment suggests the utility of the present model in the engineering design of catalytic combustors over a wide range of operating conditions.

III EXPERIMENTAL STUDIES

As pointed out by the theoretical model, for the nonadiabatic
case the exchange of heat between the ducts on the periphery of the
monolith and the surroundings makes the analysis more complex. In
order to provide a measure of the contribution of heat loss to reactor
performance we carried out a series of measurements with a single-tube
quartz reactor (Figure 1) whose inside walls were covered with platinum
dispersed on a special washcoat by means of a procedure identical to
that used in depositing noble metal on ceramic monolith reactor walls.
The Pt coated fused-quartz tube is an analog for an externally located
channel of a honeycomb monolith combustor. The catalytic section
is externally heated by an electric element to approximate the heating
by adjacent channels in an actual combustor. Instrumentation permits
determination of a number of parameters as a function of axial distance
along the catalytic tube, including wall (catalyst) temperature, gas
temperature and gas composition. The experimental variables include:
inlet gas composition, temperature, and flow velocity. Propane/air
mixtures were used in these studies.

An important problem in catalytic combustion for power generation
is the operational stability of the combustor at different power levels
and direction of operating modes. In examining this problem we carried
out experimental studies in which we assessed reactor performance at
constant fuel/air by measuring the heat release rate with increasing
and subsequently decreasing external heat input to the catalyst walls.
The net temperature rise of the catalytic wall caused by exothermic
surface combustion was monitored at a point located inside the reactor,
4.5 cm from the inlet. In Figure 2 we plot this temperature increase

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as a function of wall temperature measured in a parallel experiment
under non-reactive conditions. Curve A shows the temperature rise with
increasing external heat input and Curve B with decreasing external
heat input. The combustion has a rapid onset ("light-off") at about
500 K, raising the catalyst temperature by nearly 200 K. When external
heating has been discontinued, reaction continues to supply heat to the
wall at about the same rate until the heat balance reaches a point
corresponding to a wall temperature of about 375 K in the absence of
reaction. The observed hysteresis, the difference in external conditions
needed to ignite and extinguish the catalyzed reaction, are expected
to cause delays in combustor response to changes in input and produce
more than one level of performance for fixed input.

Successive changes in the temperature of the fuel-air mixture
entering the catalytic combustion tube modify the axial temperature
profile on the catalytic wall. In the first experiment represented by
the series of curves in Figure 3, the combustible gas mixture is propane
in air preheated to a temperature T_o = 515 K. In this case rapid
exothermic reaction occurs very near the beginning of the catalytic
section. The wall reaches and maintains a temperature of about 630 K.
At lower inlet gas temperatures the temperature of the wall rises more
gradually with respect to axial distance. However, the upper limit of
temperature attained is the same. The axial temperature profile observed
in the absence of fuel with an inlet gas temperature of 515 K is also
shown and indicates a nearly isothermal condition. The total gas flow
rate through the tube was 2 l/min in all cases. The temperature of
the wall at the inlet exceeds the gas temperature because of the heat
contribution from the external heater of the catalyst section. It is
to be noted that depending on the inlet gas temperature the heat release
rate (indicated by the slopes of the curves) due to exothermic catalytic
reaction may vary from high values close to the inlet section to a
maximum rate inside the catalytic duct.

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Similarly the axial temperature profile observed on the wall of the catalytic combustor exhibits significant changes as the fraction of fuel in the feed gas is changed (Figure 4). At low fuel fractions, the wall temperature increases gradually, reaching a plateau near the end of the catalytic wall. As the fuel fraction is increased the heat release rate increases resulting in steeper axial temperature profiles and higher temperature maxima. As the propane fraction approaches the stoichiometric fuel-air ratio, the wall temperature exhibits a pronounced peak near the inlet with a steady diminution at greater values of tube length.

The rate of consumption of fuel, as measured by the surviving fraction of fuel in the gas at the outlet of the catalytic tube (Table I) is a function of the fuel/air ratio in the inlet gas. Complete consumption of the fuel is not attained during passage of the gas through the reactor under the experimental conditions (inlet gas temperature T_o = 515 K). Also, only part of the fuel is converted to CO_2, the remainder being CO. This observation (Table I) suggests that the oxidation of propane occurs in two steps, a rapid oxidation to CO, followed by a slower oxidation to CO_2. At low fuel fractions the heat release rates are insufficient to yield high enough temperatures for CO oxidation. The exothermic heat of reaction for propane oxidation to CO ($-\Delta H^o$ = 285 kcal) is significantly lower than that for its complete oxidation to CO_2 ($-\Delta H^o$ = 489 kcal). With the inlet gas containing nearly 3 vol% propane in air, peak temperatures in excess of 750 K are attained and a larger fraction of the fuel is converted to CO_2. In this situation the contribution of homogeneous gas phase combustion may become necessary for more complete combustion.

Our results clearly demonstrate the heat loss to the environment and also to the incoming gas mixture. Analysis of these data requires some modification of the theoretical model described in the preceding section. Such an effort is currently under way.

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Table I

PRODUCT DISTRIBUTION AT OUTLET OF CATALYTIC TUBE

Volume Percent C_3H_8 in Air at Tube Inlet	Fraction of C_3H_8 Converted:		
	Total	To CO_2	To CO
0.86	0.36	0.09	0.27
1.24	0.46	0.18	0.28
1.65	0.60	0.28	0.32
2.13	0.68	0.36	0.32
2.99	0.81	0.54	0.27
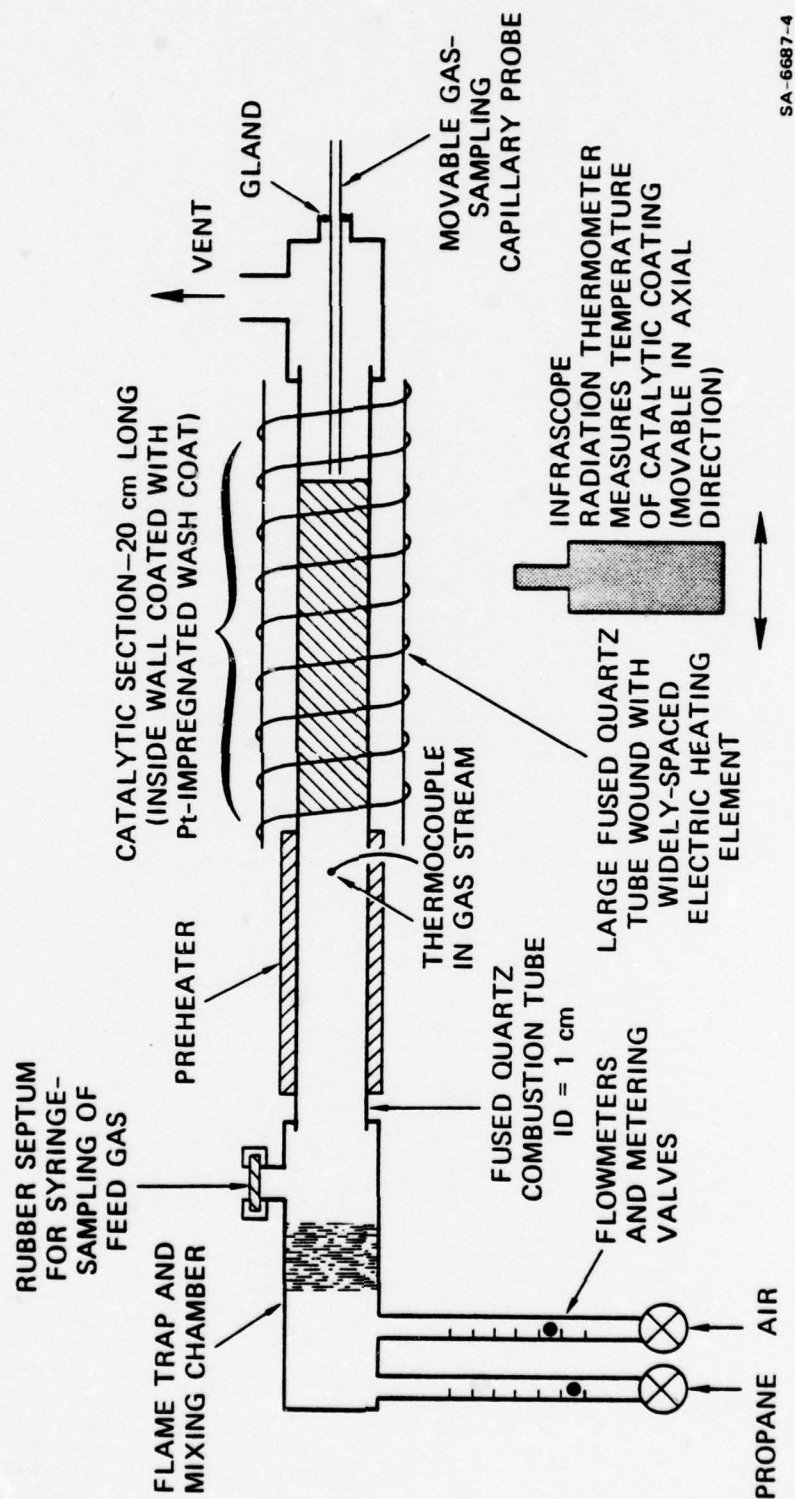
FIGURE 1   SCHEMATIC DIAGRAM OF CATALYTIC COMBUSTION APPARATUS

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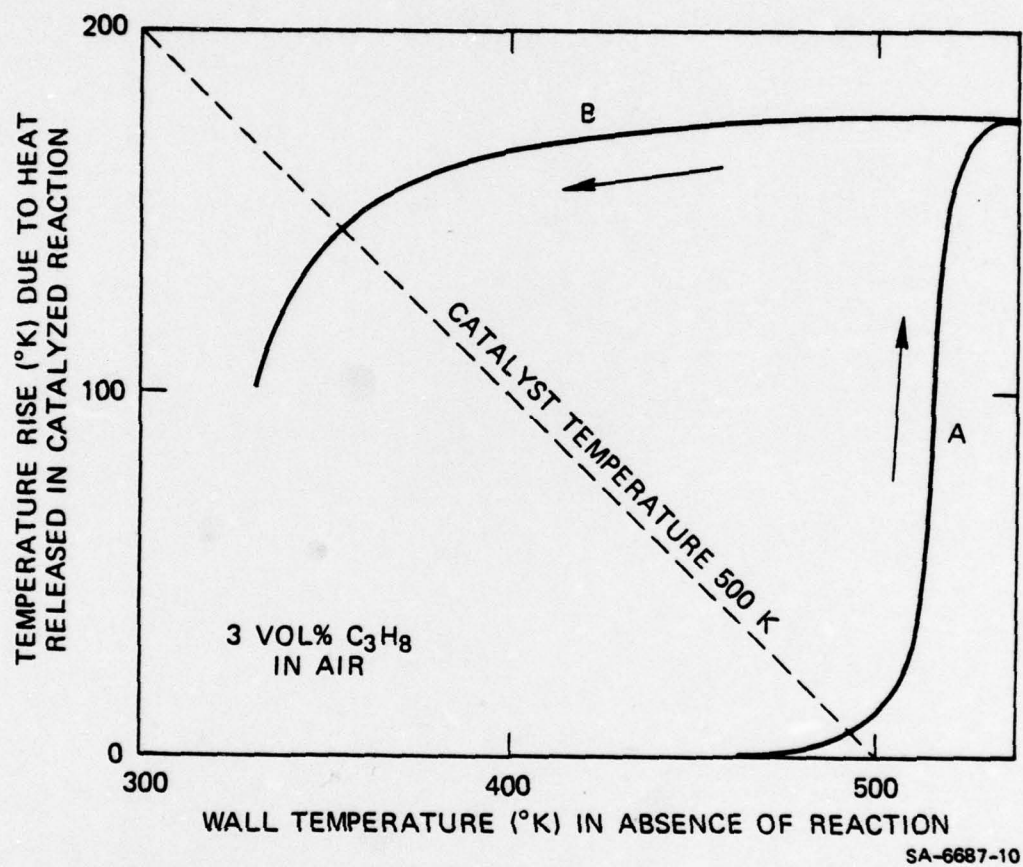
FIGURE 2   EXPERIMENTAL OBSERVATION OF CATALYTIC COMBUSTION HYSTERESIS

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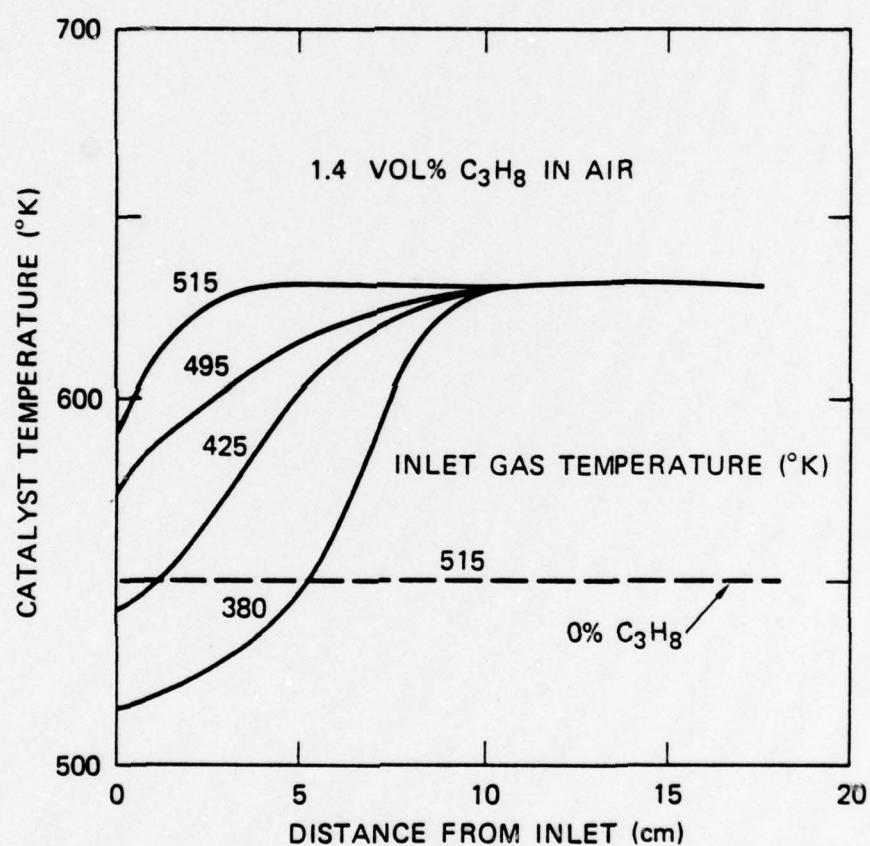
FIGURE 3   EFFECT OF INLET GAS TEMPERATURE ON CATALYTIC
WALL REACTION
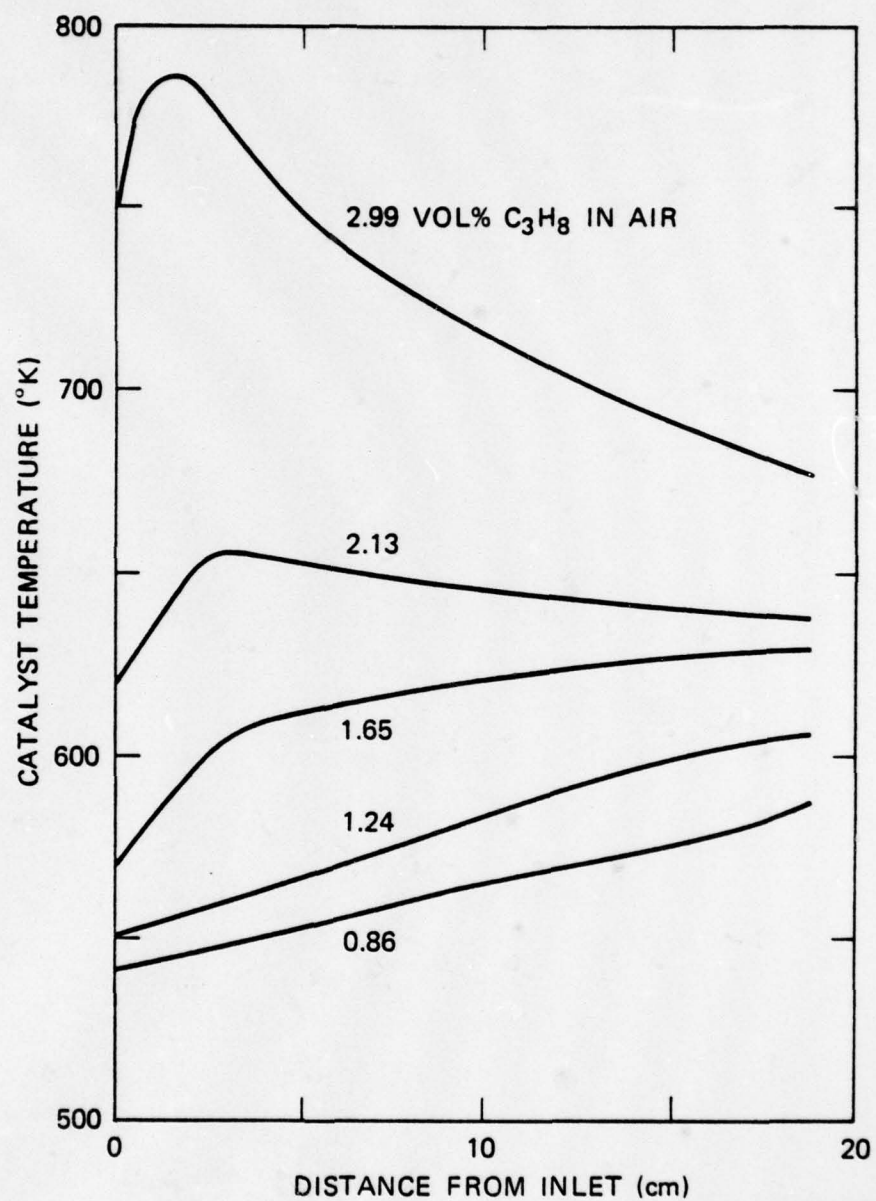
FIGURE 4   EFFECT OF FUEL-AIR MIXTURE RATIO ON CATALYTIC
WALL REACTION

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APPENDIX

Technical Report

THEORETICAL ANALYSIS OF TEMPERATURE AND
COMPOSITION IN A CATALYTIC MONOLITH REACTOR[*]

By

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ABSTRACT

A theoretical model of catalytic combustion is developed which allows calculation of temperature and reactant/product distribution in a tubular duct with catalytic walls. Under adiabatic conditions, as prevail in the central ducts of a catalytic monolith combustor, and in the absence of heat conduction along the reactor walls, the model provides an analytic solution. It exhibits the existence of multiple steady states and, for gas mixtures with low Lewis number, temperature excursion in excess of the adiabatic reaction temperature. Gas-phase reactions are shown to increase the fuel consumption in a given length of catalytic duct with corresponding changes in temperature distribution. The model is applied to a series of experimental results obtained with different fuels in tubular reactors. Satisfactory agreement is found between theoretical and experimental data when account is taken of the contribution of heat loss from the reactor to the environment. The theoretical analysis may be employed in optimizing the engineering design of monolith reactors performing over a range of operating conditions.

I INTRODUCTION

Catalytic reactors in the form of ceramic monoliths coated with catalytically active metals have been used for the conversion of low concentrations of pollutants to oxidation products. The development of catalytic reactors for the combustion of fuel-air mixtures in thruster applications[1] is receiving attention because the heterogeneous reaction can be initiated over a wide range of fuel-air ratios and can be carried to completion at temperatures sufficiently low to prevent the formation of such pollutants as nitric oxide. During the operation of such combustors, the catalytic monolith effectiveness is generally mass transfer limited,[2] i.e. the reactant species have insufficient time to diffuse to the wall and react before leaving the reactor. Under these conditions it is desirable to increase the degree of reactant conversion by homogeneous, gas-phase reactions promoted by the heat and intermediate chemical species released in a catalyzed reaction.

Theoretical studies[3,4] of monolith combustion have involved computational investigations of mathematical models of reaction and flow including temperature dependent transport and kinetic parameters. In the present work catalyzed combustion is examined by means of a simplified model.

The analysis includes heterogeneous reaction at the tube wall and homogeneous, gas phase reaction. For the low fuel/air ratios under consideration the reaction rates are taken to be of first order in fuel, and of zero order in oxygen concentration. The reaction kinetics involve global reaction rates of the Arrhenius type obtained from separate kinetic studies.

The model includes heat transfer by convection in the gas, by diffusion from the tube wall to the gas, by conduction to the surroundings, and by conduction along the tube wall. Conduction to the surroundings is negligible for ducts in the interior of a monolith where uniform conditions prevail.[5] Ducts near the periphery of the monolith are subject to heat transfer through the duct wall. Heat conduction along the tube wall is important near the duct entry where temperature gradients are high.

If heat conduction along the tube wall is neglected, as contrasted to the computer modeling employed in reference 6, the model has analytic solutions in the two cases: (a) temperature independent, diffusion controlled, heterogeneous reaction with heat transfer to the surroundings and (b) temperature dependent reaction without external heat transfer.

II DUCT FLOW MODEL

The steady-state temperature and concentration distributions in each duct cross section are modelled by their average plug flow values in the gas phase, denoted by subscript G, and their values at the catalyst surface, subscript S. The heat balance in a cross section of the fluid reads

$$R_H \frac{d}{dx} (\rho_G v \, C_G T_G) = -h_T (T_G - T_S) + R_H Q k_G \rho_G Y_G \tag{1}$$

where, for the fuel-lean case, the nearly constant concentration of oxidizer is included in the reaction rate constant k_G. The heat transfer coefficient may be expressed in terms of either the Stanton or Nusselt numbers:

$$h_T = \rho_G \mathbf{v} C_G St = (\lambda_G/4R_H) \, Nu$$

The fuel mass balance in the fluid

$$R_H \frac{d}{dx} \, (\rho_G \mathbf{v} \, Y_G) = -h_M(\rho_G Y_G - \rho_S Y_S) - R_H \, k_G \rho_G \, Y_G \quad . \tag{2}$$

The mass transfer coefficient h_M may be written in terms of the diffusion coefficient D of the fuel through the gas mixture and the Sherwood number Sh:

$$h_M = (D/4 \, R_H) \, Sh \quad .$$

The fuel that diffuses to the surface of the catalyst is consumed by the reaction:

$$h_M(\rho_G \, Y_G - \rho_S Y_S) = k_S \rho_S Y_S \quad . \tag{3}$$

Finally, heat balance in the duct wall may be written as:

$$R_w \lambda_w \frac{d^2 T_S}{dx^2} + h_T(T_G - T_S) + Q \, k_S \rho_S \, Y_S = N_w \, h_T(T_S - T_E) \tag{4}$$

where N_w is the ratio of the heat transfer coefficients for exterior and interior temperature differences.

III GOVERNING PARAMETERS

The governing parameters are found by a nondimensionalization of the equations. The dimensionless distance and temperature, ξ and τ, are taken to be

$$\xi = x \, St/R_H \quad , \quad \tau = T/\Delta T_A \tag{5}$$

where the adiabatic temperature rise ΔT_A is defined by

$$\Delta T_A = Q \, Y_{GO}/C_G \quad .\qquad (6)$$

Since $m = \rho_G v$ is a constant, Eq. (1) may be divided by $m \, C_G \, St \, \Delta T_A$ to obtain

$$\frac{d\tau_G}{d\xi} = -(\tau_G - \tau_S) + R_H Q \, k_G \tau_G \, Y_G/m \, C_G \, St \, \Delta T_A$$

Introduction of the unburned fuel fraction, y, $y = Y/Y_{GO}$, as a dependent variable and use of the constant pressure relation, $\rho_G T_G = $ constant, reduces the equation to

$$\frac{d\tau_G}{d\xi} = -(\tau_G - \tau_S) + \bar{k}_G \, y_G/\tau_G \quad , \quad \bar{k}_G = k_G \, R_H \, \rho_{GO} \, T_{GO}/m \, St \, \Delta T_A \qquad (7)$$

Similar manipulation of Eq. (2) results in

$$\frac{dy_G}{d\xi} = -(Sh/Nu \, Le) \, [y_G - (\rho_S/\rho_G) y_S] - \bar{k}_G \, y_G/\tau_G$$

where Le, the Lewis number, is defined by $Le = \lambda/\rho_G C_G D$. The analogy between heat and mass transfer, $Sh = Nu$, gives

$$\frac{dy_G}{d\xi} = -[y_G - (\rho_S/\rho_G) \, y_S]/(Le) - \bar{k}_G \, y_G/\tau_G \quad . \qquad (8)$$

Eq. (3) reduces by the same method to

$$y_G - (\rho_S/\rho_G) \, y_S = (Le) \, \bar{k}_S \, y_S/\tau_S \quad , \quad \bar{k}_S = k_S \, \rho_{GO} T_{GO}/m \, (St) \, \Delta T_A \qquad (9)$$

Finally, Eq. (4) becomes

$$(1/Pe) \frac{d^2 \tau_S}{d\xi^2} + \tau_G - \tau_S + \bar{k}_S y_S/\tau_S = N_w(\tau_S - \tau_E) \tag{10}$$

where Pe, the Peclet number, is defined by $Pe = R_H^2 h_T/R_w \lambda_w (St)^2$.

The fuel fraction y_S at the catalytic surface can be eliminated from Eqs. (7), (8), and (10) by use of Eq. (9). There remain the three following equations for the three variables y_G, τ_G, and τ_S:

$$\frac{d\tau_G}{d\xi} = -(\tau_G - \tau_S) + \bar{k}_G y_G/\tau_G \tag{11}$$

$$\frac{dy_G}{d\xi} = -F y_G - \bar{k}_G y_G/\tau_G \tag{12}$$

$$\frac{1}{Pe} \frac{d^2 \tau_S}{d\xi^2} + \tau_G - \tau_S + F y_G = N_w(\tau_S - \tau_E) \quad , \quad F = 1/(Le + \tau_G/\bar{k}_S) \tag{13}$$

Fraction F may be recognized as the factor that indicates the control of the process either by reaction kinetics, if $\bar{k}_S$ is small so that the second term dominates, or by diffusion, if $\bar{k}_S$ is large.[7]

The differential equations are to be solved under the entry conditions:

$$y_G = 1, \ \tau_G = \tau_{G0}, \ \frac{d\tau_S}{d\xi} = 0, \ \tau_S = \tau_{G0} \text{ at } \xi = 0. \tag{14}$$

For a thin ceramic wall the Peclet number, the ratio of the heat transfer coefficients for diffusion into the stream to that for conduction along the wall, will be very large. In this case the term involving Pe may be omitted from Eq. (13). This approximation lowers the order of the differential system so that two of the conditions in Eq. (14) need to be

dropped. The conditions on τ_S are the ones omitted on the physical grounds that the temperature of an insulated wall should not be prescribed. As a result of the omission of the wall heat conduction term, the model has solutions where the wall temperature jumps discontinuously from one value to another. The jumps are smoothed over to become intervals of sharp temperature variation[8] if the conduction term is reintroduced.

The equations of the model are then Eqs. (11) and (12) and

$$\tau_G - \tau_S + F\, y_G = N_w(\tau_S - T_E) \quad , \tag{15}$$

$$y_G = 1, \ \tau_G = \tau_{G0} \text{ at } \xi = 0 \quad . \tag{16}$$

IV   CATALYTIC DUCT REACTOR WITHOUT HEAT TRANSFER TO THE SURROUNDINGS

A duct in the interior of the monolith is likely to be in thermal equilibrium with adjacent ducts. The model is then applicable with $N_w = 0$, the adiabatic case. Eq. (15) becomes

$$\tau_G - \tau_S + F y_G = 0, \tag{17}$$

so that the sum of Eqs. (11) and (12) gives

$$y_G' + \tau_G' = 0$$

Integration of this differential equation gives

$$y_G + \tau_G = 1 + \tau_{G0} \tag{18}$$

where the constant of integration has been fixed by the boundary conditions in Eq. (16).

Equations (17) and (18) relate τ_G, τ_S and y_G to one another and so determine the phase space solution curves. Since either y_G or τ_G is readily eliminated from Eq. (17) by use of Eq. (18), the phase space can be represented as a two-dimensional plane. Figure 1 presents such a phase plane.

The solution curves for positive, non-dimensional reaction rate constants lie between the extremes of kinetic control where $\bar{k}_S = 0$ and diffusion control where $\bar{k}_S = \infty$. Eq. (17) shows that the two conditions correspond to the lines $\tau_S = \tau_G$ and $\tau_S = [\tau_G(Le - 1) + 1 + \tau_{G0}]/Le$, respectively. These lines and the line of the initial condition, $\tau_G = \tau_{G0}$, form a triangle in the phase plane. Points inside the triangle represent positive finite reaction rates and therefore are physically accessible. The vertices of the triangle are points I, K, and D. Point I, $\tau_S = \tau_G = \tau_{G0} + 1$, corresponds to the end of an infinitely long duct where both gas and wall have reached the adiabatic reaction temperature. Point K represents the duct entry temperatures in the absence of exothermic reaction. Point D represents the duct entry temperatures under conditions of diffusion control. A point between K and D indicates an entry condition with finite reaction rate and therefore a wall temperature between those at K and D. At point D, $\tau_S = \tau_{G0} + 1/Le$ so that temperatures above the adiabatic ($\tau_{G0} + 1$) can be attained if $Le < 1$. Such a case is indicated in Figure 1 by point D'. The solution curves plotted in Figure 1 are those for propylene/oxygen/nitrogen mixtures at several inlet temperatures, as described below.

Since the unburned fuel fraction y_G can only decrease and, by Eq. (18), τ_G can only increase continuously, conditions producing a solution curve with a maximum point cause a discontinuous wall temperature distribution. For a solution curve such as IV on Figure 1, jumps from the left branch across the middle to the right branch can occur at any point between the local maximum and minimum on the curve. Stability considerations suggest that only the two extreme cases can prevail.

Four different operating conditions can be identified: One producing
a phase plane solution curve of type IV which gives rise to wall temper-
ature distributions that may jump in either of two locations; another
producing a curve of type III that can cause a jump at the duct entry
or at a location downstream (if the part of the solution curve outside
of the triangle had been drawn in, one would see that a type III curve
is just a type IV curve with its minimum point outside the triangle);
a condition (type II) that produces a jump at entry since both the
maximum and minimum of the complete solution curve lie outside the triangle;
and conditions of type I with no maximum or minimum. Since the jumps in
each case are from a branch of the solution curve near side K-I, to one
near D-I, the jump may be regarded as a sharp transition of the wall
reaction from kinetics to diffusion control. For conditions producing
curves of type I without a maximum or minimum, a smooth transition or no
transition at all is obtained.

Equation (11) has been integrated under the assumption of no gas phase
reaction $\bar{k}_G = 0$, for three cases and the results plotted in Figure 2. A
comparison of curves II and III shows the effect of inlet temperature on
a given gas mixture. Conditions for curves IA and III differ mainly in
fuel concentration.

An interesting deduction from the above analysis is that the phase is
independent of the homogeneous reaction. In this adiabatic case, the
relation between temperature and concentration is independent of what
fraction of the reaction is homogeneous and what is heterogeneous. The
gas phase reaction enters the calculations when the distance coordinate
for each phase is being obtained, by use of Eq. (11). The importance
of gas phase reaction may therefore be gauged by plotting to $\bar{k}_G\, y_G / \tau_G$,
a function of τ_G against $(\tau_S - \tau_G)$. Since $(\tau_S - \tau_G)$ can be read directly
from Figure 1 as the distance between the solution curve and the line K-I,
a convenient function to plot is $\bar{k}_G\, y_{FG} / \tau_G + \tau_G$ as a function of τ_G. Where

this latter graph comes near or crosses the solution curve, gas phase reaction makes a major contribution. The homogeneous reaction curve for case IB is plotted in Figure 1. Since quantitative kinetic data on the gas phase oxidation of propylene of the temperatures of interest is not available we have estimated the preexponential factor and activation energy for the homogeneous reaction to be 10^{12} sec^{-1} and 30 kcal/mol. One sees in the figure that homogeneous reaction does influence the reactive flow beyond the point where 60% of the fuel has been consumed.

The parameter plane of the inlet conditions, the temperature and adiabatic reaction temperature of the gas mixture, has been presented in Figure 3. The plane is divided to show the regions where conditions giving rise to the various types of solution curves are found. In region I the curve of τ_G as a function of τ_S given by Eq. (15) has no inflexion point with zero or negative slope. In the other regions the corresponding phase plane solution curves have such inflexion points along with a local maximum point and a minimum point. Both of these points lie outside the triangle for parameters of region II, the maximum is in the triangle for parameter points in region III, and both extreme points are in the triangle of physically real points for initial conditions in parameter region IV.

V EFFECT OF HEAT TRANSFER BETWEEN DUCT AND SURROUNDINGS

Ducts near the outer periphery of a monolith combustor lose heat to their surroundings. This heat transfer appears in the model as a non-vanishing parameter N_w in Eq. (15).

An analytic solution can be obtained in the diffusion-controlled fast wall reaction limit in the absence of homogeneous reaction. The solution reads

$$\tau_S - \tau_E = Ay_G + By_G^{N_w Le/(1 + N_w)}$$

$$A = (1 - Le)/Le[1 + N_w(1 - Le)]$$

$$B = -A + [1 + Le(\tau_0 - \tau_E)]/Le(1 + N_w) \tag{19}$$

$$\tau_G - \tau_E = (\tau_S - \tau_E)(1 + N_w) - y_G/Le \tag{20}$$

$$y_G = e^{-\xi/Le} \tag{21}$$

Equations (19) and (20) present the phase space solution. Elimination of τ_S from Eq. (20) by use of Eq. (19) gives

$$\tau_G - \tau_E = Cy + (1 + N_w)By^{N_w Le/(1 + N_w)} \quad,$$

$$C = -1/[1 + N_w(1 - Le)] \quad. \tag{22}$$

The solution is then represented by two curves, one from Eq. (19) for τ_S as a function of y and one from Eq. (22) for τ_G.

The general solution with finite wall reaction rate and with homogeneous reaction may be obtained by numerical integration of the differential equations of the models, Eqs. (11), (12), (15), and (16).

VI APPLICATION

The model has been applied to analyze some experimental results[10] in which the wall and gas temperatures were measured during steady-state catalytic combustion of fuel/oxygen/nitrogen mixtures in monoliths with a small number of ducts with catalytic walls, heated externally to the adiabatic reaction temperatures. Most of the experimental data for propylene combustion were found to fall into the diffusion-controlled reaction regime using the transport and reaction-rate parameters applicable to this system. Consequently the analytic solution given by Eqs. (19), (20), and (21) was employed. The theoretical curves based on the adiabatic

model (no heat transfer) were found to be in good agreement with the experimental data when account was taken of conductive heat loss from the reactor to the environment (Figure 4).

With hydrogen as a fuel the reaction system has a small Lewis number (Le < 1). Under these conditions the theoretical analysis predicts wall temperatures that exceed the adiabatic reaction temperature (T_A). Indeed the experimental data (Figure 5) exhibit a temperature maximum, well in excess of T_A. Theoretically, a wall temperature maximum at the reactor entrance is calculated with a monotonic decline along the reactor tube. Again the discrepancy in the temperature profile near the entrance is ascribed to heat conduction along the duct wall.

It is of interest that in calculating the temperature distribution the available kinetic data for catalytic oxidation of hydrogen have a higher degree of uncertainty than for the case of propylene oxidation. In our analysis we increased the Arrhenius preexponential factor by 10^4 over that published in reference 12, to take account of the higher degree of dispersion of Pt on the monolith-washcoat support. With the reaction and transport parameters listed in Table I, the experimental data obtained for this system were found to be in the diffusion-controlled reaction region.

VII CONCLUSIONS

A theoretical model of reactive flow through a duct with catalytic walls has been developed that by means of an analytical solution provides estimates of temperature and fuel product distributions in catalytic combustion in the absence of heat transfer to the environment. The model provides a direct way of assessing the importance of the contribution of the gas phase reaction, and a prediction of the length of duct required to reach a specific temperature and fractional fuel conversion.

The phase space derived from the model relates the concentrations and temperatures at the wall and in the stream that can occur together in each duct cross section. These relations are found to be independent of the homogeneous reaction and of the flow rate. However the distance into the duct where a particular phase is reached depends on the flow rate and degree of homogeneous reaction.

In the adiabatic case, valid for ducts in the interior of a monolith, the analytic solution is found to be confined to a certain triangle in the wall temperature-gas temperature phase plane. The vertex of the triangle is the point where wall and gas reach the adiabatic reaction temperature. The base of the triangle is on the line where the gas temperature has its inlet value and extends from the point of equal wall and gas temperatures to a wall-gas temperature difference inversely proportional to the Lewis number. Thus high wall temperatures are to be expected at the duct entry for gas mixtures with low Lewis number. The surprising fact that temperatures in excess of the adiabatic reaction temperature can be attained is due to this result.

For an adiabatic reacting system with known initial concentration of fuel, oxidizer, and inert diluent, the inlet parameters are the gas inlet temperature and the temperature rise for adiabatic reaction. Different forms of temperature variation along the duct are found for different parameter ranges. Solutions with jump discontinuities down-stream of the duct entry are obtained from parameters represented by points in a certain quadrant of the parameter plane (Figure 3). A cold gas mixture with relatively high fuel content (high adiabatic reaction temperature) introduced into the reactor, will favor temperature jumps and multiple steady states. The model also suggests that the contribution of homogeneous relative to heterogeneous reaction will increase with larger monolith tube diameter.

Nomenclature

C	specific heat (cal/g-deg)
D	diffusion coefficient (cm/sec^2)
F	Frank-Kamenetskii factor, Eq. (26)
h_M	mass transfer coefficient (cm/sec)
h_T	heat transfer coefficient (cal/cm^2-sec-deg)
$\bar{k}$	nondimensional reaction rate constant
k_G	gas phase reaction rate constant (sec^{-1})
k_S	catalyzed surface reaction rate constant (cm/sec)
Le	Lewis number
m	mass flux (g/cm^2 sec)
Nu	Nusselt number
N_w	ratio of heat transfer coefficients
Pe	Peclet number
Q	heat released by reaction (cal/gm)
R_H	hydraulic radius (cross sectional area divided by perimeter, cm)
R_w	thickness of the duct wall (cm)
Sh	Sherwood number
St	Stanton number
T	temperature ($^\circ$K)
ΔT_A	temperature rise of adiabatic reaction ($^\circ$C)
v	flow velocity (cm/sec)
x	distance from duct entry (cm)
Y	fuel mass fraction
y	ratio of Y to Y at duct entry
λ	thermal conductivity (cal/cm-deg-sec)
ρ	density (g/cm^3)
μ	viscosity (poise)
ζ	nondimensional distance
τ	ratio of temperature to ΔT_A

Subscripts

O   at the duct entry

E   exterior of the duct

G   in the gas phase

S   at the solid surface of catalyst

w   in the duct wall

REFERENCES

1. W. C. Pfefferle, R. W. Carrubba, R. M. Heck, and G. W. Roberts, "Catathermal Combustion, A New Process for Low-Emissions Fuel Conversion," ASME paper 75-WA/Fu-1.

2. T. J. Rosfjord, "Catalytic Combustors for Gas Turbine Engines," AIAA paper 76-46.

3. A. E. Cerkanowicz, R. B. Cole, and J. G. Stevens, "Catalytic Combustion Modeling; Comparisons with Experimental Data," ASME paper 77-GT-85.

4. J. T. Kelly, R. M. Kendall, E. Chu, and J. P. Kesselring, "Development and Application of the PROF-HET Catalytic Combustion Code," paper 77-33, Western States Section/The Combustion Institute, Stanford, October 1977.

5. S. M. DeCorso, S. Mumford, R. V. Carrubba, and R. Heck, "Catalysts for Gas Turbine Combustors - Experimental Test Results," J. Eng. for Power, Vol. 99A, 159-167 (1977).

6. J. Votruba, J. Sinkule, V. Hlavacek, and J. Skrivanek, "Heat and Mass Transfer in Monolithic Honeycomb Catalysts - I., Chem. Eng. Sci., Vol. 30, 117-123 (1975).

7. D. A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics, Plenum Press, New York (1969).

8. G. Eigenberger, "On the Dynamic Behavior of the Catalytic Fixed-Bed Reactor in the Region of Multiple Steady States - I. The Influence of Heat Conduction in Two-Phase Models," Chem. Eng. Sci., Vol. 27, 1909-1916 (1972).

9. R. A. Svehla, "Estimated Viscosities and Thermal Conductivities of Gases at High Temperatures," NASA TR R-132 (1961).

10. L. L. Hegedus, "Temperature Excursions in Catalytic Monoliths", AIChE J., Vol. 21, 849-853 (1975).

11. S. Goldstein, Modern Developments in Fluid Dynamics, Oxford (1938).

12. R. Schefer, R. Cheng, F. Robben, and N. Brown, "Catalyzed Combustion of H_2/Air Mixtures on a Heated Platinum Plate," presented to Western States Section/The Combustion Institute, Boulder (1978).

13. Handbook of Chemistry and Physics (1936).

14. A. Schwartz, L. L. Holbrook, and H. Wise, "Catalytic Oxidation Studies with Platinum and Palladium," J. Catalysis, Vol. 21, 199-207 (1971).

Table I

NUMERICAL VALUES FOR THE CALCULATIONS

Quantity	Propylene	Hydrogen	Reference
Fuel/oxygen/nitrogen (vol%)	0.19/5.08/94.73	1.90/4.60/93.50	10
ΔT_A (°C)	119.	150.	10
T_{GO} (°C)	417.	260	10
T_E (°C)	536	410	
Re	967.	1175.	10
Le	1.554	0.326	10
R_H (cm)	0.0368	0.0368	10
R_W (cm)	0.041	0.041	10
Nu	6.	6.	11
Pr	0.75	0.75	9
St = Nu/Re Pr	8.27×10^{-3}	6.81×10^{-3}	
λ_W (cal/cm-sec-°C)	10^{-3}	10^{-3}	13
λ_G for N_2 at 700°K (cal/cm-sec °C)	1.2×10^{-4}	1.2×10^{-4}	9
μ_G for N_2 at 700°K (poise)	3.2×10^{-6}	3.2×10^{-6}	9
Pe	19.5	23.7	
Preexponential factor A_W (cm/sec)	10^{8*}	1.4	12
Activation energy E_W (kcal/mol)	22.0	3.85	14,12
$m = \mu Re/4R_H$ (gm/cm^2 sec)	0.0210	0.0255	
$\rho_{GO}T_{GO}$ g/cm^3	0.351	0.3395	
$\bar{k}_S$ at 700°K	254	1.16	

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*Value large enough for diffusion controlled first-order reaction, although negative order reactions were observed.[14]
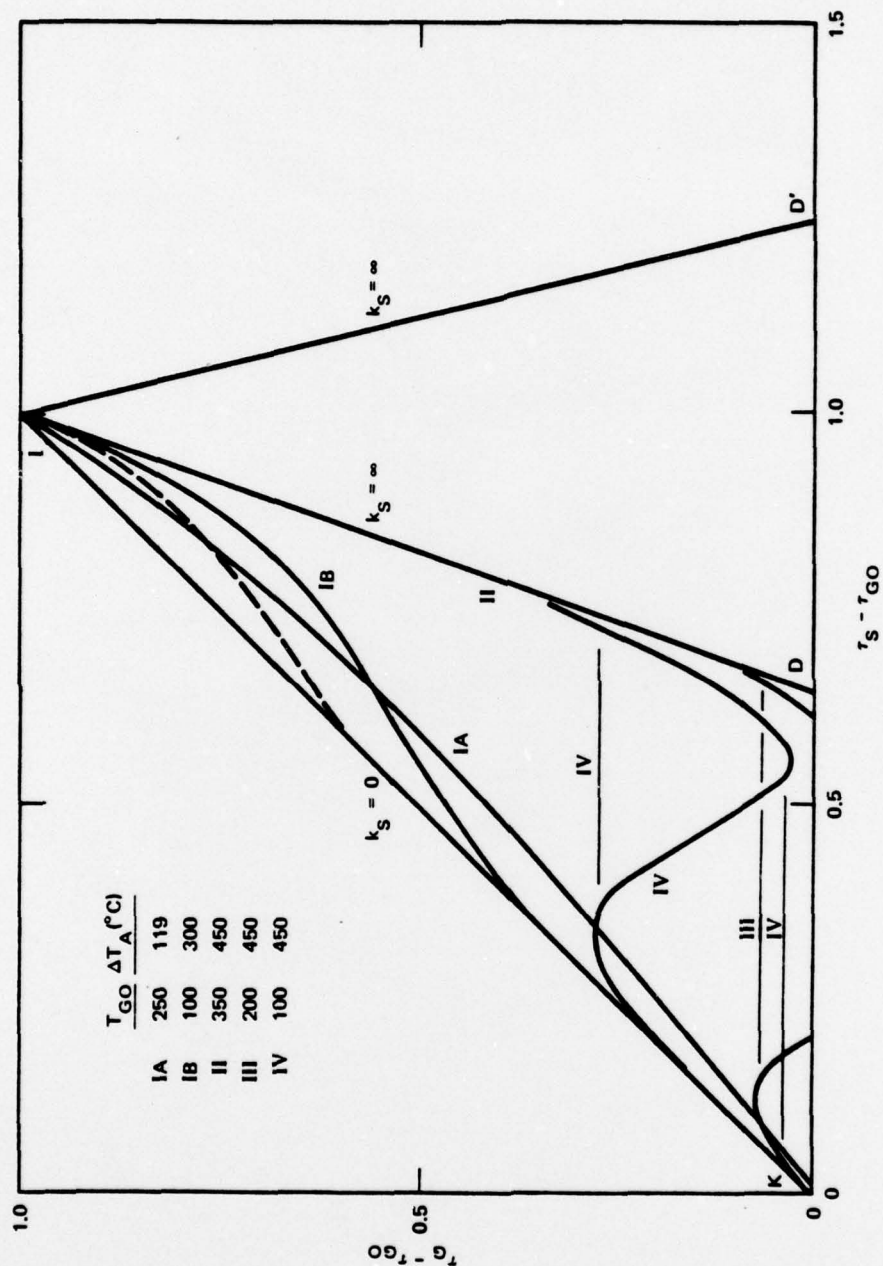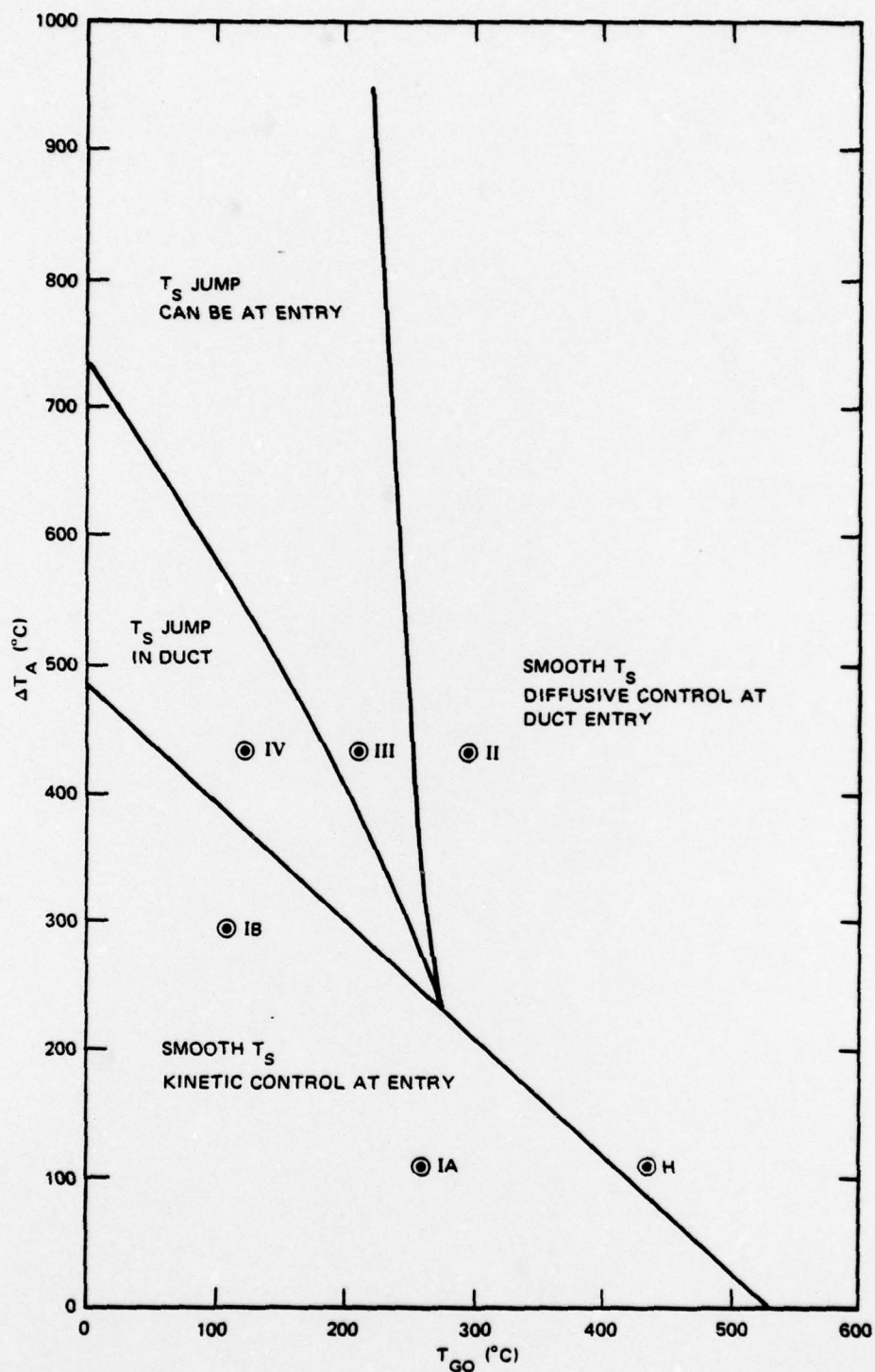
FIGURE 1   PHASE PLANE THEORETICAL CURVES FOR PROPYLENE/OXYGEN/NITROGEN MIXTURES: $y_F = 1 - (\tau_G - \tau_{GO})$; $N_W = 0$; - - - homogeneous reaction for Case IB.
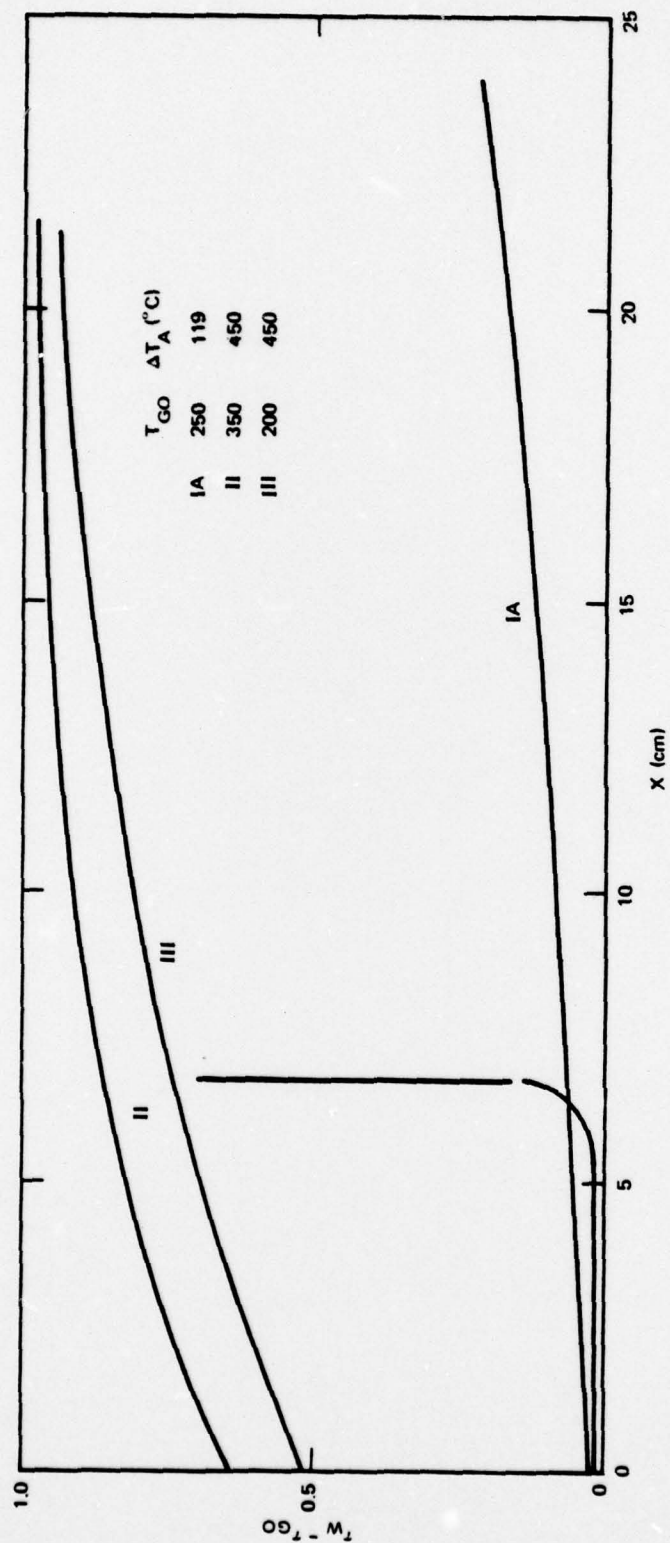
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FIGURE 2   THEORETICAL NON-DIMENSIONAL WALL TEMPERATURES PLOTTED AGAINST DISTANCE FROM DUCT ENTRY FOR A FEW PROPANE/OXYGEN/NITROGEN MIXTURES FLOWING AT Re = 967 IN A DUCT WITH R_H = 0.0368 CM

FIGURE 3 THEORETICAL REACTIVE FLOW REGIMES FOR PROPYLENE/OXYGEN/NITROGEN MIXTURES. POINT H FOR DATA REF. 10.
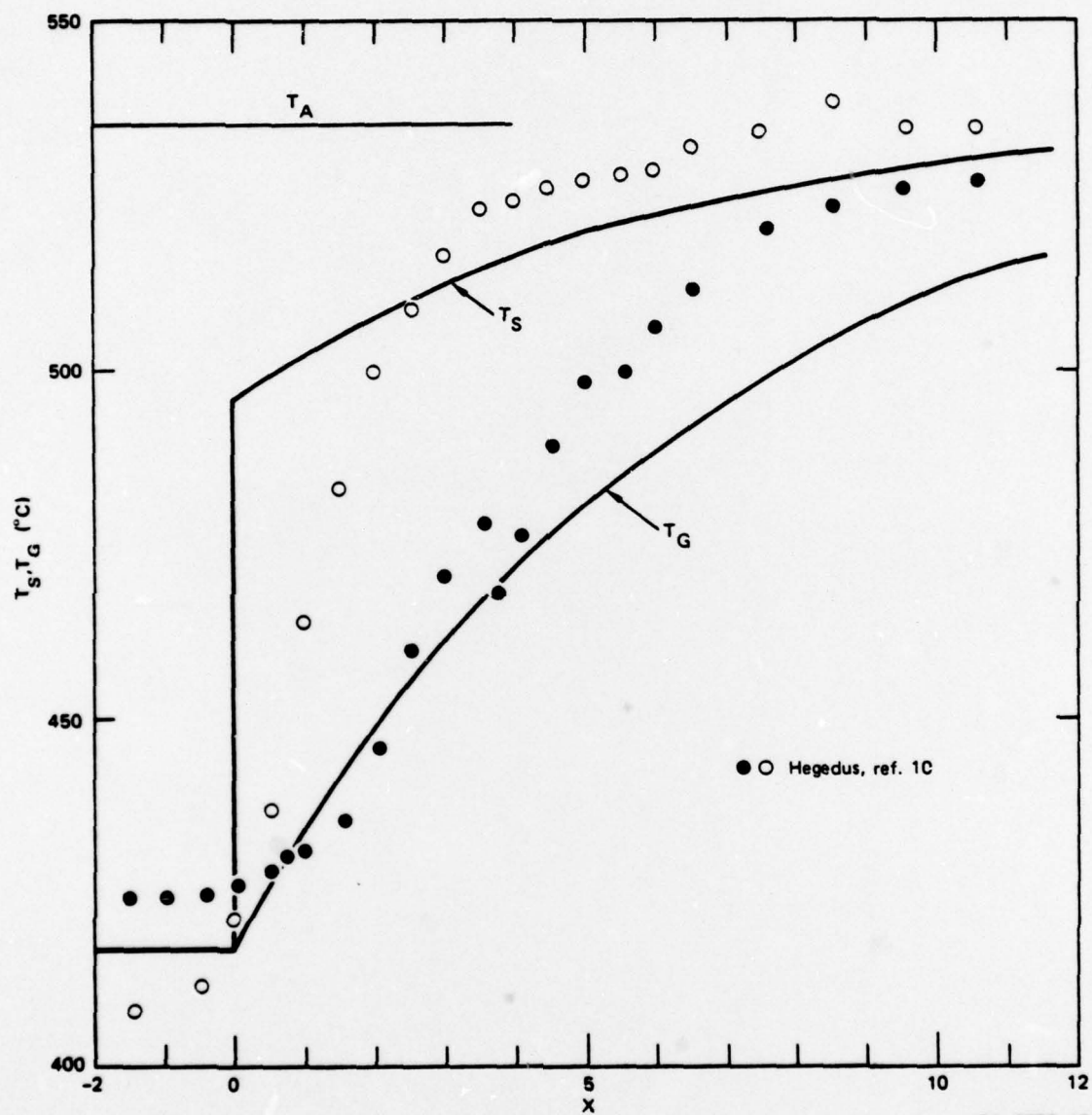
FIGURE 4   PHYSICAL PLANE FOR $C_3H_6/O_2/N_2$ MIXTURE.   THEORETICAL CURVES WITH $k = 10^8 \exp(-22,000/RT)$, $N_W = 0.2$.
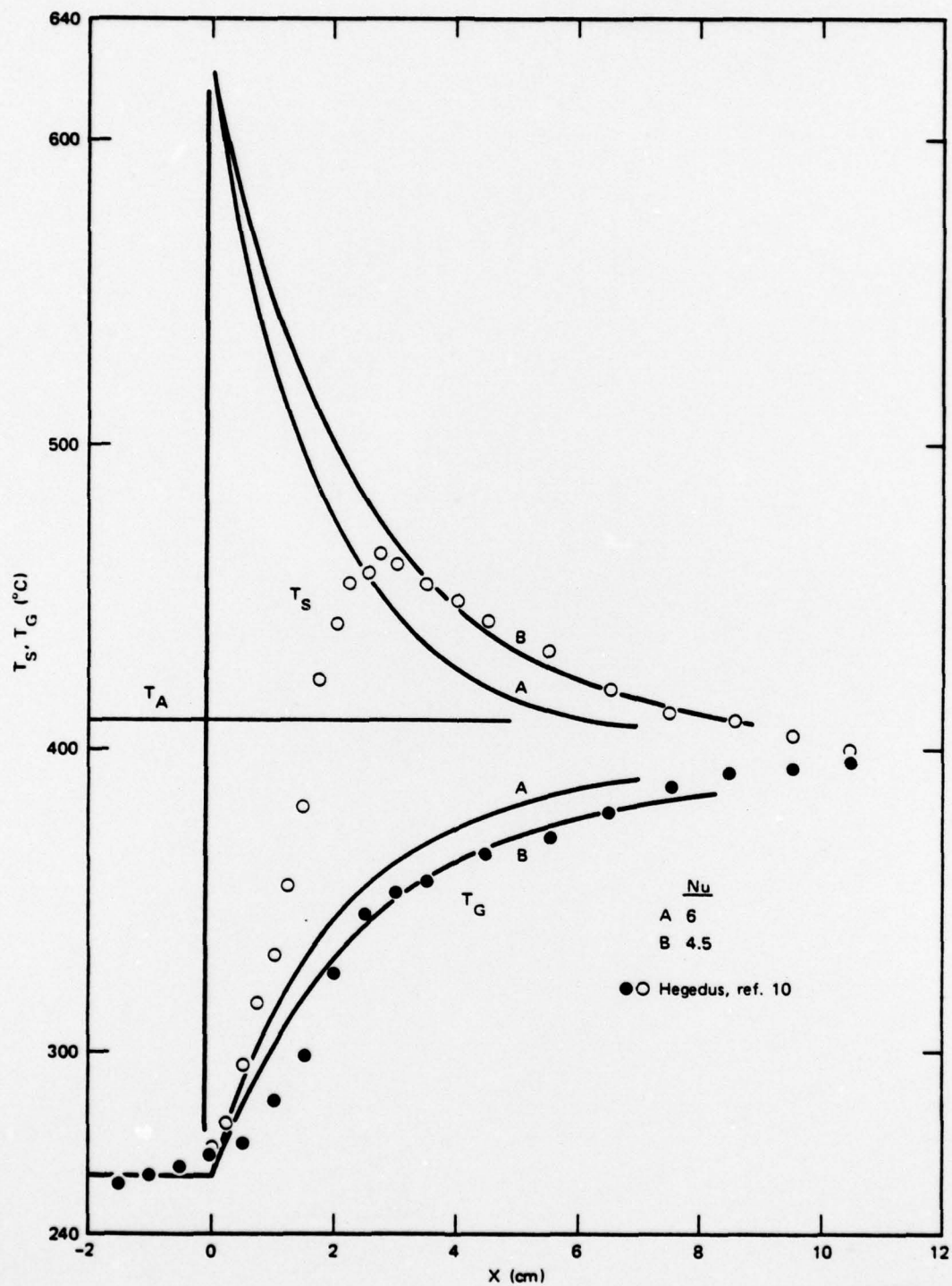
FIGURE 5   PHYSICAL PLANE FOR $H_2/O_2/N_2$ MIXTURE. CURVES COMPUTED WITH
$k = 3.2 \times 10^3$ exp (-3850/RT) N_W = 0.2.

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The research effort has for its objectives a detailed analysis of those parameters that affect the catalytic combustion of fuel-air mixtures in a monolith combustor, and of the contribution of gas phase reactions to catalytic combustor performance. A theoretical analysis and experimental study have been carried out of reactive flow with exothermic reaction on

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20. (Abstract)

the catalytic walls of a tubular reactor. The model allows calculation of temperature and reactant/product distributions in a tubular duct with catalytic walls based on experimentally measured heterogeneous reaction rates. Under adiabatic conditions, as prevail in the central ducts of a catalytic monolith combustor, and in the absence of heat conduction along the reactor walls, an analytic solution can be obtained. The solution shows the existence of multiple steady states and, for gas mixtures with low Lewis number, temperature excursions in excess of the adiabatic reaction temperature. Operating conditions are identified under which gas-phase reactions can make significant contributions by increasing the fuel consumption in a given length of catalytic duct with corresponding changes in temperature distribution and gas-phase composition. The model is applied to a series of experimental results obtained with different fuels in tubular reactors. Satisfactory agreement is found between theoretical and experimental temperature distributions for a monolith combustor operating under nearly adiabatic conditions. When account is taken of the contribution of heat loss from the reactor to the environment, we are able to apply the analysis to catalytic combustion under nonadiabatic conditions, as encountered in single ducts or at the periphery of a monolith combustor. The theoretical analysis may be employed in optimizing the engineering design of monolith reactors performing over a range of operating conditions.